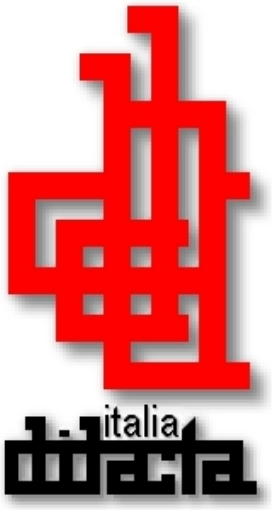
Didacta Italia

IC14D

Water Conditioning Plant

User's Manual

and Exercise Guide



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IC14D

Water Conditioning Plant

User's Manual

and Exercise Guide

This manual illustrates the technical characteristics and operating instructions of the system Didacta IC14D Water Conditioning Plant, giving the instructor or the student a specific knowledge of the unit and its applications. Besides the manual contains a choice of exercises ready to be performed in the laboratory.

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Printed in Italy - 15/11/10

Code 01903E1202 – Edition 01 - Revision 01

Table of Contents

1. General 1

2. System Components and Description 3

2.1 Composition 3

2.2 Description 4

2.2.1 Control panel 5

2.2.2 Agitators 9

2.2.3 Flow control 10

3. Start-Up and Maintenance 13

3.1 Starting the system 13

3.1.1 pH instrument 13

3.1.2 rH instrument 13

3.2 Maintenance 14

3.2.1 pH probe 14

3.2.2 Calibrating the pH probe 15

3.2.3 pH - rH Electrode regeneration 16

4. Exercises 17

4.1 Experience no. 1 - Chromate removal (galvanising plants) 17

4.2 Experience no. 2 - Cyanide removal (galvanising plants) 19

4.3 Experience no. 3 - Trivalent chromate removal (tanning plants) 21

4.4 Experience no. 4 - Influence of the nature of the polyelectrolyte in the flocculation process 22

4.4.1 Execution of the test 24

4.5 Experience no. 4 - Influence of the pH of the medium on the flocculation process 25

4.5.1 Execution of the test 25

4.6 Experience no. 6 - Influence of the quantity of polyelectrolyte on flocculation 26

4.6.1 Execution of the test 26

4.7 Experience no. 7 - Influence of the degree of dilution of the polyelectrolyte on the flocculation process 27
4.7.1 Execution of the test 27
4.8 Experience no. 8 - Influence of the simultaneous variation of type of polyelectrolyte and ph of the medium on the flocculation process 28
4.9 Experience no. 9 - Chemical evaluation of pollutants contained in the water before and after the treatment plant 29
4.10 Experience no. 10 - Dosing hexavalent and trivalent chrome 31
4.11 Experience no. 11 - Crystallisation studies 35

1. General

As its immediate consequence, technological progress has brought about an unbalance in the chemical-biological composition of natural waters.

The need to discharge industrial effluents, in fact, represents a very severe ecological problem, since such effluents contain - in greater or lesser quantities - substances that are harmful to man, animals and plants.

These pollutants affect the people that use natural water courses for drinking purposes, terrestrial animals that find in rivers and lakes their natural sources of drinking water, as well as the river and lake fauna and flora that may be poisoned, whether directly or indirectly, by such by-industrial products.

As a first approximation, industrial effluents can be subdivided into two major groups:

- effluents basically consisting of organic products
- effluents containing substances of inorganic origin.

The former reduce the quantity of oxygen dissolved in the water, which results in the fauna dying for lack of air, while the others have toxic effects and represent veritable poisons in the traditional understanding of the term.

Many pollutants belong to both groups: some organic substances, in fact, consume the oxygen contained in the water and are also toxic; inorganic substances erode the oxygen because of their reducing action.

Other forms of pollution are due to settling and suspended compounds. Aside from an accessory toxic effect, the former tend to settle on the bottom of water courses and damage the local flora thereby hampering the regular formation of plankton; the latter make the water turbid thereby preventing the penetration of sunlight and slowing down chlorophyll photosynthesis.

The best way to prevent the severe consequences of pollution obviously consists of preventing all types of contaminants from being discharged into natural water courses.

This can be obtained by processing all effluents with treatment plants designed to bring the composition of the effluents into line with applicable standards.

Obviously, it is not possible to design a single treatment plant that will handle all types of effluent. Process selection is a decision of the utmost importance, requiring a preliminary study that takes into account all the factors involved case by case.

It is impossible to identify beforehand all the pollutant factors associated with each single effluent, because each case is a unique instance and therefore cannot be viewed as a standard of universal validity.

However, the effluents to be treated can be assigned to major categories as a function of their origin.

Since treatment plants represent a major cost for manufacturing plants, these systems should be studied in detail, so as to enable future technicians to familiarise with their working principles and be able, in future to select the most appropriate systems case by case. This knowledge is necessary to the people responsible for designing, operating or maintaining the water treatment plants.

To this end, DIDACTA ITALIA has designed and created IC14D as an indispensable teaching and testing aid for the problems to do with the clarification of industrial service waters.

The most dangerous effluents from galvanising plants basically consist of cyanides and chromates. In the latter case, toxicity is eliminated through reduction in the acid field; for cyanides it is achieved through oxidation in the alkali field. Similar pollution phenomena are due, among others, to effluents from tanning plants, oil refineries, chemical and food processing plants, wine makers.

2. System components and description

If your system differs from the one described below, see Annex "1" to this manual

2.1 Composition

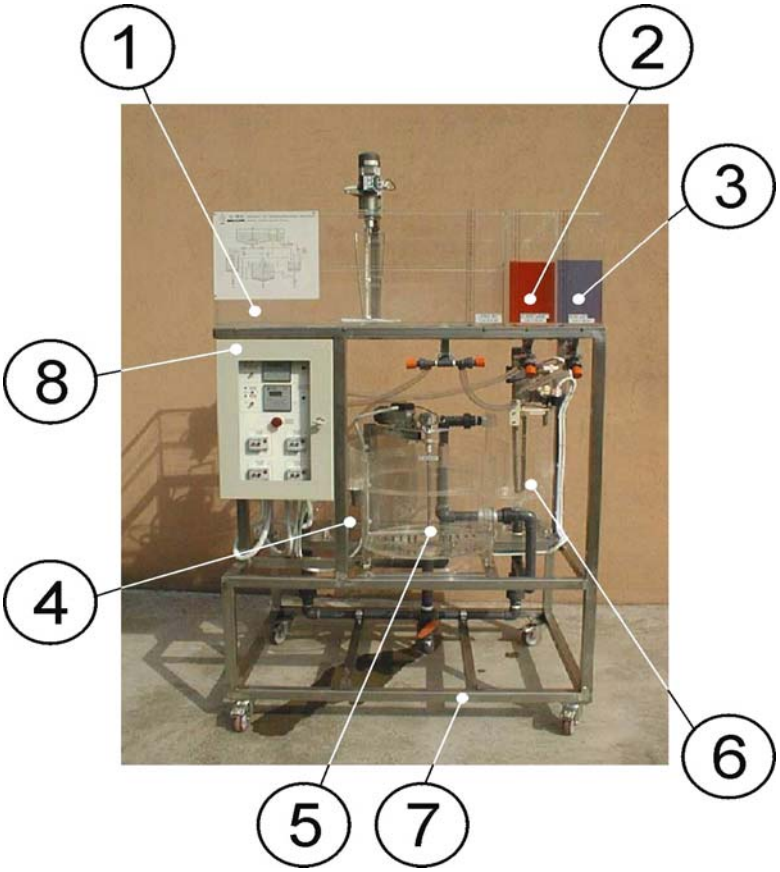

Fig. 2.1 - Overall view of the system

1. ***170 lt. mixture preparation tank, in polished clear polymethacrylate, with graduation for volumetric filling, with electrically operated agitator.***
2. ***23 lt. tank for oxidising or reducing agent, in polished clear polymethacrylate with graduation for volumetric filling.***
3. ***23 lt. tank for acids or bases, in polished clear polymethacrylate with graduation for volumetric filling.***
4. ***23 litre oxidation or reduction tank in polished clear polymethacrylate, with electrically operated agitator.***
5. ***70 lt. settling tank, with DORR sludge conveyor, in polished clear polymethacrylate.***
6. ***23 lt. neutralisation tank polished clear polymethacrylate, with electrically operated agitator.***
7. ***Wheeled stainless steel frame for easy handling in the laboratory.***
8. ***Control and monitoring electric panel with protections, fuses, indicator lights, main switch and control buttons.***

2.2 Description

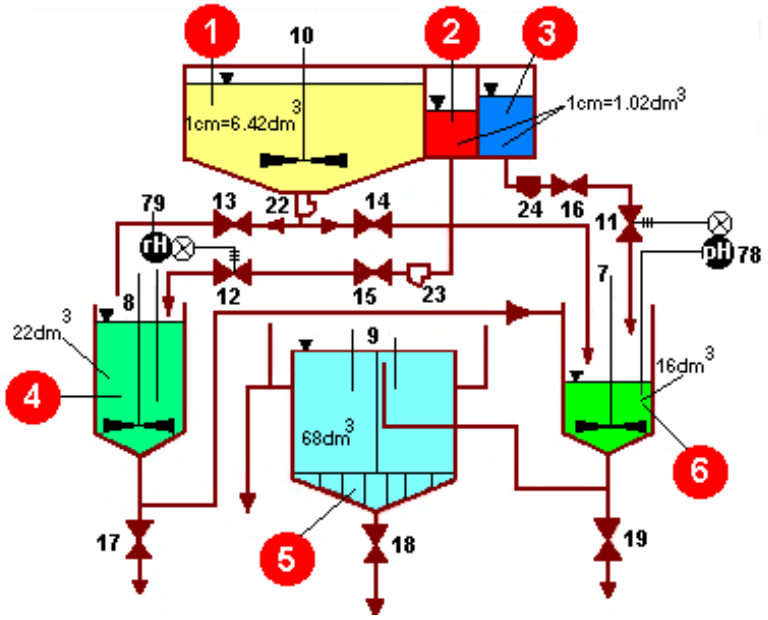

Fig. 2.2 - Synoptic view of system

1. *Feed tank*
2. *Oxidising/reducing agent tank*
3. *Acid/base tank*
4. *Oxide/reduction tank*
5. *Settling tank*
6. *Neutralisation tank*
7. *Agitator - tank 6*
8. *Agitator - tank 4*
9. *Agitator - tank 5*
10. *Agitator - tank 1*
11. *Acid/base solenoid valve*
12. *Oxide/reduction solenoid valve*
13. *Feed valve - tank 4*
14. *Feed valve - tank 6*
15. *Oxide/reduction control valve*
16. *Acid/base control valve*
17. *Discharge valve - tank 4*
18. *Discharge valve - tank 5*
19. *Discharge valve - tank 6*
22. *Filter - tank 1*
23. *Filter - tank 2*
24. *Filter - tank 3*
78. *pH-meter*
79. *rH-meter*

The water to be treated is prepared in tank (1) by adding the pollutants specified for the test. By means of the control valves (13), the water is transferred into the oxide/reduction tank (4) where the reactant is made to enter through the opening of valve (15) and solenoid valve (12), which, in its turn, is governed by the rH (79) control instrument. After that, the water is transferred to the neutralisation tank (6) to which the precipitating/neutralising agent contained in tank (3) is added, and whose quantity is controlled by valve (16) and by the pH control instrument (78) which works on solenoid valve (11). In the neutralisation tank (6), in order to activate the precipitation process, it is possible to add a flocculant element. This is dosed by means of a special graduated glass vessel equipped with a faucet. Finally, the water reaches the settler (5) which separates the water from the sludge: the clarified water going to the discharge pipes comes out from the top of the settler, while the sludge comes out from the bottom via a ball valve (18). A by-pass valve (14) makes it possible to transfer the water directly from the feed tank (1) to the neutralisation tank (6) when the water to be treated only contains trivalent chrome, as is generally the case in effluents from tanning plants.

2.2.1 Control panel

If your electrical control panel differs from the one described below, see Annex "1" to this manual.

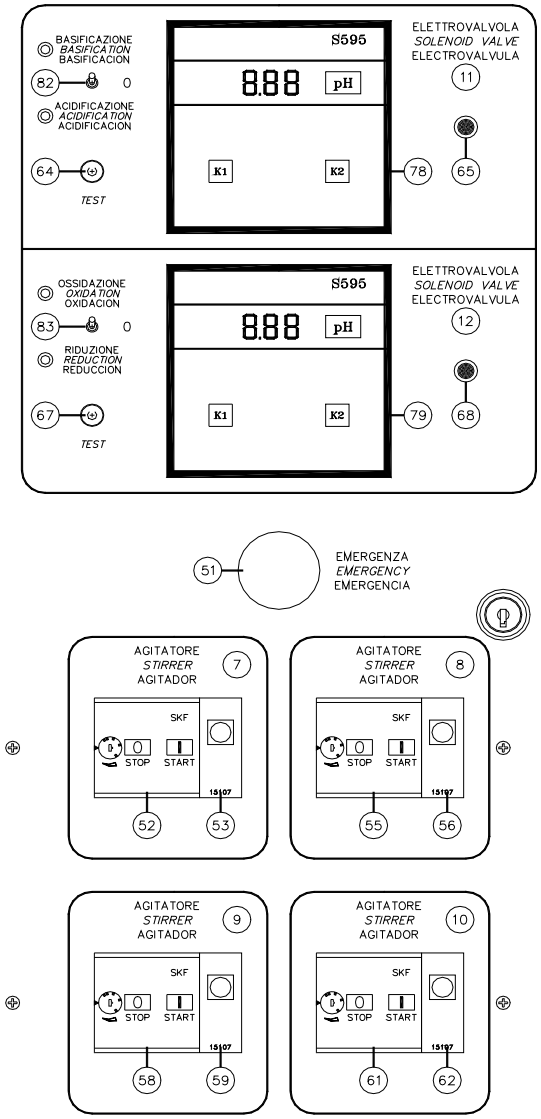

Fig. 2.3 - Control panel

7. Tank 6 agitator control
8. Tank 4 agitator control
9. Tank 5 agitator control
10. Tank 5 agitator control
11. Tank 1 agitator control
12. pH solenoid valve control
51. Emergency button
52. Agitator 7 magnetothermal switch
53. Agitator 7 indicator light
55. Agitator 8 magnetothermal switch
56. Agitator 8 indicator light
58. Agitator 9 magnetothermal switch
59. Agitator 9 indicator light
61. Agitator 10 magnetothermal switch
62. Agitator 10 indicator light
64. pH solenoid valve test button
65. pH solenoid valve indicator light
67. rH solenoid valve test button
68. rH solenoid valve indicator light
78. pH control instrument
79. rH control instrument
82. Basification/acidification selector
83. Oxidation/reduction selector

2.2.1.1 pH- meter (ref. 78 fig. 2.3)

Fig. 2.4 - pH controller

Panel mounted instrument for the measurement and control of pH, with 3½ digit LCD. The standard version has a 0/4 - 20 mA output for signal transmission to remote units and two ON/OFF control outputs, one of which is timed. In addition to the input from the pH electrode, there is a thermocompensation input.

The very high impedance signal, in mV, generated by the electrode is amplified and converted into a 0 - 2V signal. Amplification involves asymmetry control (by means of the ZERO trimmer) and gain control (GAIN trimmer). The 0 - 2V signal is then transmitted to the A/D converter of the display, to the output stage in current for conversion to 0/4 to 20 mA, and to the controllers stage, where the signal is compared with the thresholds so as to obtain the conditions of the output relay. A solenoid valve for the dosage of the corrective solution is connected to this relay (see fig. 2.6).

Characteristics:

Measuring range	0 - 14 pH
Input	from pH electrode
Accuracy	> 0.3 % f.s.
Repeatability	> 0.2 % f.s.
Output in current	0 -20 / 4-20 mA on max load of 700Ω
ON-OFF controllers	Two mutually independent relays with exchange contact, max. capacity 3A at 220V AC, resistive.
Timing of relay K1	From one to 15 minutes, in one-minute steps, set by means of a dip-switch on panel front.

Calibrating the thresholds:

1. Press the reading button of relay 1 and read the setting on the display; to change it, work on the relative trimmer (turn it clockwise to increase it, counter-clockwise to reduce it).

2. Press the reading button of relay 2 and work on the relative trimmer to change the setting.

3. When the two buttons are released, the values reappear on the display.

The “threshold exceeded” and “relay energised” conditions are indicated by the relative LEDs on the front panel.

If no timing has been set, the **THRESHOLD** LED and the K1 **RELAY** LED light up and go out at the same time.

2.2.1.2 rH-meter (ref. 79 fig. 2.3)

Fig. 2.5 - rH controller

Panel-mounted instrument for the measurement and control of the redox, with 3½ digit LCD. The standard version has a 0/4 - 20 mA output for signal transmission to remote units and two ON/OFF control outputs, one of which is timed. In addition to the input from the pH electrode, there is a thermocompensation input.

The very high impedance signal, in mV, generated by the electrode is amplified and converted into a 0 - 2V signal. Amplification involves asymmetry control (by means of the ZERO trimmer) and gain control (GAIN trimmer. The 0 - 2V signal is then transmitted to the A/D converter of the display, to the output stage in current for conversion to 0/4 to 20 mA, and to the controllers stage, where the signal is compared with the thresholds so as to obtain the conditions of the output relay. A solenoid valve for the dosage of the corrective solution is connected to this relay (see fig. 2.6).

Characteristics:

Measuring range	0 to 1000 mV or -500 to 500 mV
Input	from redox electrode
Accuracy	> 0.3 % f.s.
Repeatability	> 0.2 % f.s.
Output in current	0 - 20 / 4 - 20 mA on max. load of 700Ω
ON-OFF controllers	Two mutually independent relays with exchange contact, max. capacity 3A at 220V AC, resistive.
Timing of relay K1	From one to 15 minutes, in one-minute steps, set by means of a dip-switch on panel front.

Calibrating the thresholds:

1. Press the reading button of relay 1 and read the setting on the display; to change it, work on the relative trimmer (turn it clockwise to increase it, counter-clockwise to reduce it).

2. Press the reading button of relay 2 and work on the relative trimmer to change the setting.

3. When the two buttons are released, the values reappear on the display.

The “threshold exceeded” and “relay energised” conditions are indicated by the relative LEDs on the front panel.

If no timing has been set, the **THRESHOLD** LED and the K1 **RELAY** LED light up and go out at the same time.

Fig. 2.6 - Detail of neutralisation tank solenoid valve (11)

2.2.2 Agitators

Fig. 2.7 - Agitator 10 with impeller in stainless steel (100 rpm).

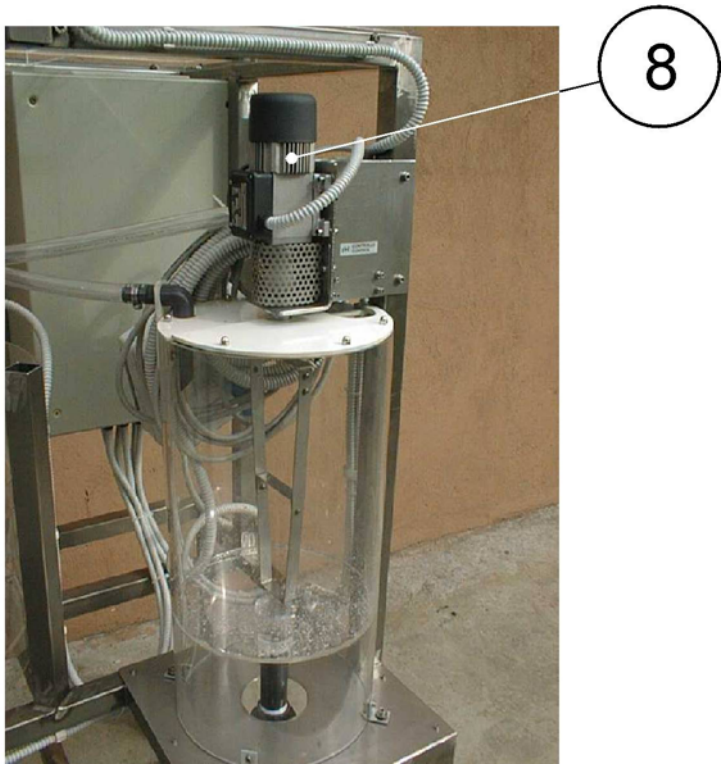

Fig. 2.8 - Agitator 8 with impeller in stainless steel (100 rpm).

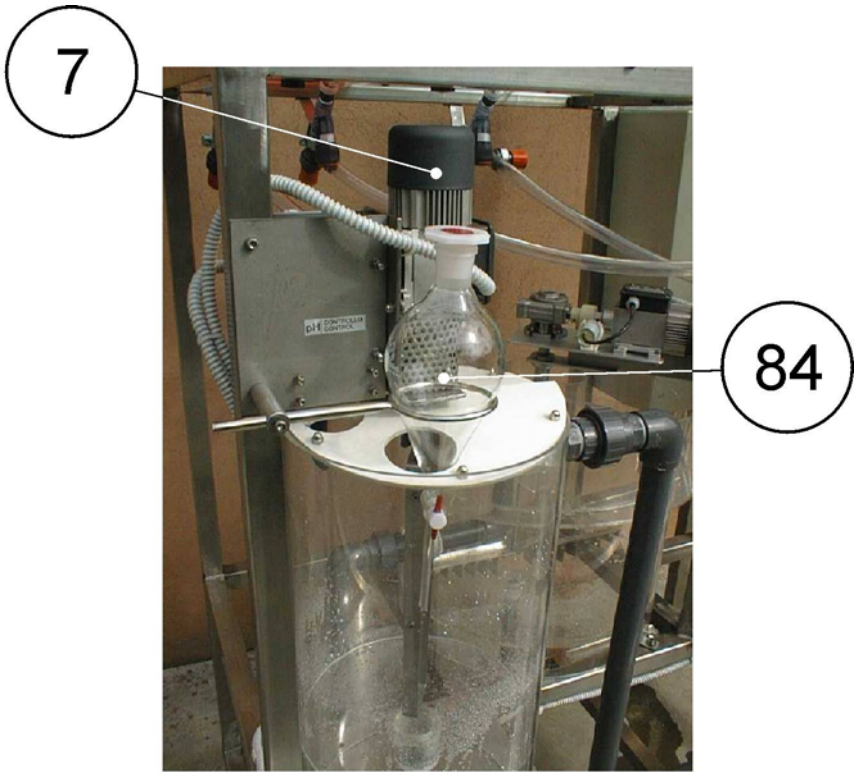

Fig. 2.9 - Agitator 7 with impeller in stainless steel (100 rpm) and flocculant flask.

Fig. 2.10 - Agitator 9 in stainless steel with DOOR type rake blades (2 rpm).

2.2.3 Flow control

The system is not equipped with instruments for the direct reading of flow rate. To control flow, work on the valves shown in figure 2.8. Flow can be adjusted as necessary by means of a chronometer (not supplied) and the graduated scales applied to the tanks.

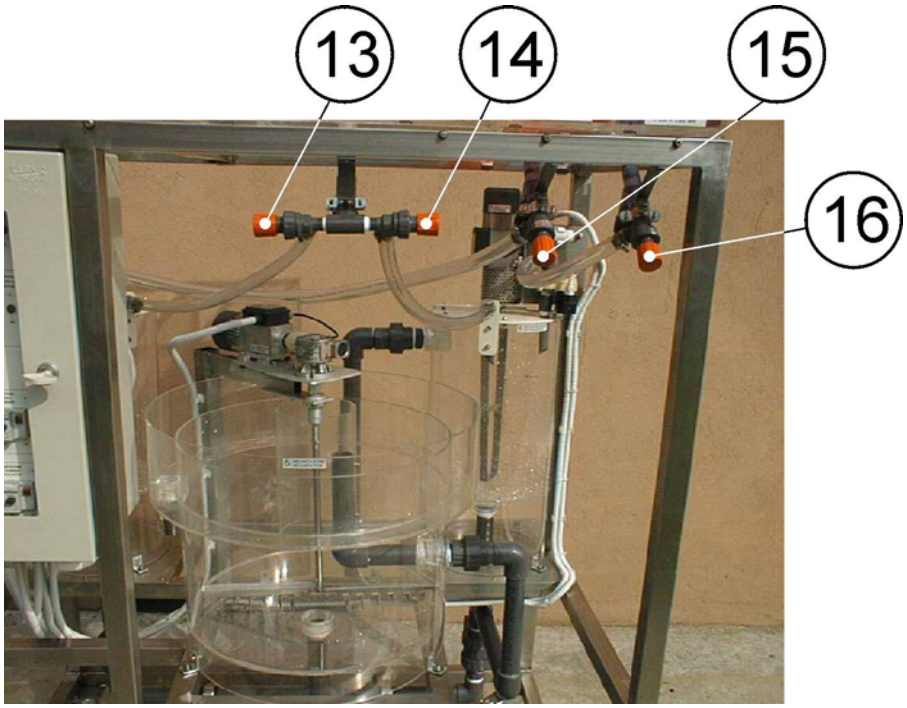

Fig. 2.11 - Flow control detail

13. Valve for flow control from tank 1 to tank 4

14. Valve for flow control from tank 1 to tank 6

15. Valve for oxidant/reducer flow control

16. Valve for acid/base flow control

Product flow to the settling tank (ref. 5 fig. 2.1) depends on the sum of the flow rates from the feed tank (ref. 1 fig. 2.1), the oxide/reduction tank (ref. 2 fig. 2.1) and acid/base tank (ref. 3 fig. 2.1).

3. Start-up and maintenance

3.1 Starting the system

System start-up is very simple, just follow the steps listed below.

1. Conned the system to the power mains as shown on the control panel.
2. Connect the discharge pipe (fig. 3.1) the laboratory's water discharge system.
3. Check the functionality of the pH and rH instruments.

Fig. 3.1 - Discharge manifold

3.1.1 pH instrument

Set the selector (ref. 82 fig. 2.3) on basification, place a sample of acid liquid in a container (add hydrochloric acid) and introduce the pH probe, set the instrument on set-point 8, check whether indicator light (ref. 65 fig. 2.3) lights up (solenoid valve open), add a small quantity of sodium hydroxide to make the liquid basic and wait until the indicator light (ref. 65 fig. 2.3) goes out (solenoid valve closed). Always check with litmus paper the readings given by the instrument.

3.1.2 rH instrument

Set the selector (ref. 83 fig. 2.3) on reduction, place a sample of acid liquid in a container (add hydrochloric acid – potassium dichromate - pH 3) and introduce probe rH, check whether indicator light (ref. 68 fig. 2.3) lights up (solenoid valve open) and

check set-point +100 mV, add a small quantity of metabisulfite to reduce the chrome (the colour changes from yellow to green) and wait until the indicator light (ref. 68 fig. 2.3) goes out (solenoid valve closed). The reading on the digital indicator changes from 400 mV to ca 100 mV. Always check the values given by the instrument with sample solutions.

N.B.

Before starting the system we recommend wearing protective clothing, gloves and goggles in order to avoid contact with corrosive substances. Always comply with local regulations on the use and handling of corrosive substances.

Before discharging any substance into the laboratory's discharge system make sure that the substance has been neutralised. Comply with the applicable regulations on the disposal of chemical substances.

3.2 Maintenance

At the end of each exercise, empty out and clean the tanks. The pH and rH probes must be treated as described below.

3.2.1 pH probe

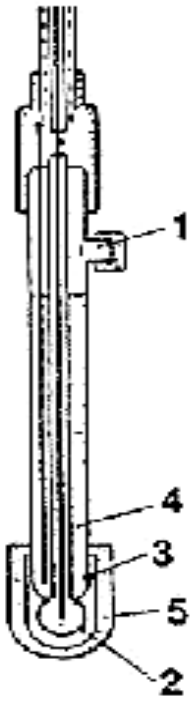

Fig. 3.2 - pH probe

Protect the plug and cable splices against humidity.

The electrodes must be kept scrupulously clean and free of grease; when they are not used, they must be kept under distilled water, or preferably in a KCl - 3M solution.

During transport and storage they must be protected with a special rubber cap (5) filled with the same solution; remove the cap to take the measurements. The level of the electrolyte (4) must not drop below 20 mm from the feed hole (1).

Electrodes mounted on an armature without reserve must not be submerged by more than 200 mm.

A summary cleaning of the sensitive part of the electrode must be performed *at least once a week* by rubbing it gently with a paste consisting of water and a slightly abrasive degreasing factor, and then rinsing it thoroughly.

Alkaline encrustations can be readily eliminated by submerging the part in a standard strong acid solution.

Obstructions in the porous membrane (3) due to silver sulphide deposits (dark colouring) are eliminated with an appropriate detergent (Ingold 9892 or equivalent).

3.2.2 Calibrating the pH probe

The equipment must be calibrated periodically and whenever an electrode is replaced: this is indispensable because the characteristics of sensitivity and the "0" point of the electrodes vary as a function of type, use and time.

This operation must be repeated at a greater or lesser frequency in relation to the accuracy required.

Proceed as follows:

1. Rinse the electrode and remove any encrustation;

2. To reactivate the membrane (2) (this is necessary especially after a prolonged period of inactivity) by submerging the electrode first in a 1% - 2% solution of HF (Ingold 9895 or equivalent) for 30 seconds and, immediately afterwards, in distilled water, for at least 12 hours;

3. Remove and fit back the plug of the lateral filling hole (1) to equilibrate the inner pressure with the outside pressure;

4. Eliminate any air bubbles from inside the membrane (2);

5. Pour the buffer solutions, pH 7 and pH 4 or 9, into two plastic cups, with capacity of ca 10 ml. each (this is done not to waste an excess quantity of the buffer solutions, which must not be salvaged);

6. Rinse the electrode with distilled water and submerge it in the pH 7 solution until the porous membrane is covered;

7. Stir for 5 seconds, wait at least 10 seconds and work on the "ZERO" adjustment until the reading corresponds to the pH of the butter at that temperature (buffer solutions are supplied with a table listing the pH values at different temperatures);

8. Remove the electrode from the solution, rinse it with distilled water and submerge it into the pH 4 or pH 9 solution and, observing the times described above, work on the "GAIN" trimmer until the reading corresponds to the pH value assumed by the buffer solution at that temperature;

9. Repeat these steps at least a couple of times, always rinsing the electrode in distilled water before passing from one solution to another.

3.2.3 pH – rH electrode regeneration

When an electrode has crystal particle at the tip, it has to be regenerated; also make sure that the electrode is also filled with liquid.

Prepare a saturate solution of potassium chloride + distilled water ($KCl + H_2O$), submerge the electrode in distilled water to dissolve the salts, empty out the solution from the electrode, wash the electrode with distilled water and fill it up with the $KCl + H_2O$ solution.

4. Exercises

4.1 Experience no. 1 – Chromate removal (galvanising plants)

Of all the pollutants contained in galvanising plant effluents we have selected those generating the worst forms of contamination, i.e. hexavalent chrome and alkali cyanides.

Hexavalent chrome is contained in the effluents of galvanising plants in an acid environment and hence the chromate/dichromate balance

$$2\ Cr0_4^{--} + 2H^+ \leftrightarrow Cr_2\ 0_7^{--} + H_2O$$

fosters the formation of dichromates.

The treatment process includes several steps:

- checking the pH of the water to be treated;
- reducing Cr^{6+} to Cr^{3+} with bisulphite, according to the following reactions

$$Cr_2\ 07^{--} + 3HSO_3^- + 5H^+ \leftrightarrow 2Cr^{3+}\ 3SO_4^{--} + 4H_2O;$$

- neutralising the water;
- precipitation of Cr^{3+} in a slightly alkaline environment (through the addition of a flocculant agent to make the flocs bigger);
- sedimentation of $Cr\ (OH)_3$;
- discharging the clarified water;
- discharging the sludge.

The operations to be performed on the system are:

a) Fill tank 1 to about three quarters (ca 70 litres), add ca 200 cc of sulphuric acid in a 20% solution and by means of litmus paper make sure that pH value is approx. 2; add 10 gr. of potassium dichromate so as to obtain a concentration of 50 ppm of Cr^{6+} in the 70 litres of water poured into the tank.

b) Switch selector (61) on ON to start agitator 10; agitator activation is indicated by lighting of the corresponding telltale (62).

c) Analyse the water to determine the titre of hexavalent chrome.

d) Open valve 13 to direct the flow into tank 4.

e) Prepare the reducing solution to be transferred into tank 2; keep in mind that for stoichiometric purposes, 100 gr. of potassium dichromate require 105 g of sodium bisulphite and the latter is originated by dissolving metabisulphite in water according to the following reaction:

$$Na_2S_20_5 + H_2O \;\; 2NaHS0_3$$

to reduce all the dichromate added to the initial 70 litres of water it takes 10.5 g of bisulphite, corresponding to 9.5 g of metabisulphite. Accordingly, for tank 2 we may prepare 10 litres of 0.2% solution of metabisulphite (it is always a good idea to have an excess quantity of reactant on hand).

f) Prepare the neutralising solution with 10 litres of 1% sodium hydroxide solution and transfer it into tank 3.

g) Adjust the rH indicator/controller/transmitter instrument (79) on the control panel to a set-point of 110 mV.

h) Adjust the pH indicator/controller/transmitter instrument (78) on the control panel to a set-point of 8.5.

i) Switch selector (55) on ON to start agitator 8; agitator activation is indicated by lighting of the corresponding telltale (56).

j) Gradually open valve 15.

k) In this manner the reducing agent is transferred from tank 2 to tank 4 in the amount required by the rH instrument (79); its transfer is revealed by the lighting of the relative telltale (68).

l) Switch selector (52) on ON to start agitator 7; agitator activation is indicated by lighting of the corresponding telltale (53).

m) Gradually open valve 16; when the liquid moves from tank 4 to tank 6, wait until the pH electrode is submerged in the solution. In this manner, the alkaline solution is transferred from tank 3 to tank 6 in the amount required by the pH instrument (78); its transfer is indicated by the lighting of the relative telltale (65).

n) Switch selector (58) on ON to start agitator 9, whose activation is indicated by lighting of the corresponding telltale (59), while the transfer of the turbid fluid from tank 5 to the settling tank is visible.

o) Monitor sludge settling and the outflow of clarified water.

p) Take a sample of clarified water and perform a chemical analysis on it to determine pH and check for the presence of chrome.

q) Open valve 18 and discharge the sludge.

r) Take a sample and perform a chemical analysis to determine the percentage of dry matter in the sludge.

4.2 Experience no. 2 - Cyanide removal (galvanising plants)

Of all the pollutants contained in galvanising plant effluents we have selected those generating the worst forms of contamination, i.e. hexavalent chrome (exp. no. 2) and alkaline cyanides.

Cyanides are present in an alkaline solution and are subjected to an oxidising treatment by means of hypochlorite in a markedly basic environment.

Reaction time varies depending on pH and in order to keep it within technically acceptable limits it is necessary to work at pH > 12.

Active chlorine, which is contained in the hypochlorite solution, reacts with the cyanides according to the following reaction:

$$CN^- + C1_2 \leftrightarrow CN\,C1 + c1^-$$

The cyanogen chloride that is formed initially is converted into cyanate:

$$CN\,C1 + OH^- \leftrightarrow CNO^- + H^+ + c1^-$$

Then, cyanate reacts with the hypochlorite ions according to the following reaction:

$$H_2O + 2\,CNO^- + 3\,cl^-\,0^- \rightarrow 2CO_3^{--} + N_2 + 3\,cl^- + 2H^+$$

The treatment process includes several steps:

- checking the pH of the water to be treated;
- oxidising the cyanides with hypochlorite
- neutralising the water;
- sedimentation of any noxious substances contained in the water
- discharging the clarified water;
- discharging the sludge, if any.

The operations to be performed on the system are:

a) Fill tank 1 to about ¾ (circa 70 l), add ca 300 cc. 10% sodium hydroxide solution and with the aid of litmus paper make sure that pH value is about 12; add 9 gr. of potassium cyanide so as to obtain a concentration of 50 ppm in the 70 litres of water poured into the tank.

b) Switch selector (61) on ON to start agitator 10; agitator activation is indicated by lighting of the corresponding telltale (62).

c) Analyse the water to determine the titre of cyanide.

d) Open valve 13 to direct the flow into tank 4.

e) Prepare the oxidant solution to be transferred into tank 2; keep in mind that it takes ca 50 gr. of sodium hypochlorite to oxidise the 9 gr of potassium cyanide employed; we recommend preparing 10 l of a 1% solution (it is always a good idea to have an excess quantity of reactant).

f) Prepare the neutraliser solution, to consist of 10 l of 1% H_2SO_4 solution, and transfer it into tank 3.

g) Adjust the rH indicator/controller/transmitter instrument (79) on the control panel to a set-point of 200 mV.

h) Adjust the pH indicator/controller/transmitter instrument (78) on the control panel to a set-point of 7.0.

i) Switch selector (55) on ON to start agitator 8; agitator activation is indicated by lighting of the corresponding telltale (56).

s) Gradually open valve 15.

j) In this manner the oxidant is transferred from tank 2 to tank 4 in the amount required by the rH instrument (79); its transfer is revealed by the lighting of the relative telltale (68).

k) Switch selector (52) on ON to start agitator 7, whose activation is indicated by lighting of the corresponding telltale (53).

l) Gradually open valve 16; when the liquid moves from tank 4 to tank 6, wait until the electrode is submerged in the solution. In this manner, the acid solution is transferred from tank 3 to tank 6 in the amount required by the pH instrument (78); its transfer is indicated by the lighting of the relative telltale (65).

m) Switch selector (58) on ON to start agitator 9, whose activation is indicated by lighting of the corresponding telltale (59), while the transfer of the turbid fluid from tank 5 to the settling tank is visible.

n) Monitor sludge settling and the outflow of clarified water.

o) Take a sample of clarified water and perform a chemical analysis on it to determine pH and check for the presence of cyanides.

t) Open valve 18 and discharge the sludge, if any.

p) Take a sample and perform a chemical analysis to determine the percentage of dry matter in the sludge.

4.3 Experience no. 3 - Trivalent chromate removal (tanning plants)

Tanning plants discharge huge volumes of water containing different pollutants, of both organic and inorganic nature. Among these, we have selected the chrome coming from mineral tanning baths, which is present in the form of trivalent chrome in a markedly acid environment.

The treatment process includes several steps:

- checking the pH of the water to be treated;
- neutralising the water;
- precipitation of Cr^{3+} in a mildly alkali environment
- sedimentation of $Cr(OH)_3$;
- discharging the clarified water;
- discharging the sludge.

The operations to be performed on the system are:

a) Fill tank 1 with waters to about three quarters of its capacity (ca 70 litres), add ca 200 cc of sulphuric acid in a 20% solution and by means of litmus paper make sure that pH value is approx. 2; add 35 gr. of chrome alum so as to obtain a concentration of ca 50 ppm of Cr in the 70 litres of water poured into the tank.

b) Switch selector (61) on ON to start agitator 10; agitator activation is indicated by lighting of the corresponding telltale (62).

c) Analyse the water to determine the titre of trivalent chrome.

d) Open valve 14 to direct the flow into tank 6.

e) Prepare the neutraliser solution, to consist of 10 l of 1% sodium hydroxide solution and transfer it into tank 3.

f) Adjust the pH indicator/controller/transmitter instrument (78) on the control panel to a set-point of 8.5.

g) Switch selector (52) on ON to start agitator 7; agitator activation is indicated by lighting of the corresponding telltale (53).

h) Gradually open valve 16.

i) Wait until the pH electrode is submerged in the solution. In this manner, the alkalising solution is transferred from tank 3 to tank 6 in the amount required by the pH instrument (78); its transfer is indicated by the lighting of the relative telltale (65).

j) Switch selector (58) on ON to start agitator 9, whose activation is indicated by lighting of the corresponding telltale (59), while the transfer of the turbid fluid from tank 5 to the settling tank is visible.

k) Monitor sludge settling and the outflow of clarified water.

l) Take a sample of clarified water and perform a chemical analysis on it to determine pH and check for the presence of chrome.

m) Open valve 18 and discharge the sludge.

n) Take a sample and perform a chemical analysis to determine the percentage of dry matter in the sludge.

4.4 Experience no. 4 - Influence of the nature of the polyelectrolyte in the flocculation process

Repeat Experience no. 1 up to the precipitation step: at that point, add a polyelectrolyte solution to tank 6.

This is done manually to be able to modify as desired the parameters affecting the flocculation process and hence be able to identify/detect optional conditions.

Limited to addition of polyelectrolyte, flocculation is a function of:

- nature of the polyelectrolyte
- pH of the medium
- quantity of polyelectrolyte
- degree of dilution
- add-in rate

accordingly, it is advisable to perform a number of tests changing the afore-mentioned parameters one at a time and then in combination, according to logical and reasonable criteria.

The effectiveness of the flocculation process can be assessed by determining settling velocity and/or from the dry concentration of sludge.

Therefore, it is possible to construct a number of charts in which we can plot one of these values as a function of the parameter that we intend to vary.

The polyelectrolytes commonly employed as flocculation adjuvants can be grouped into three basic types:

- cationic
- anionic

- non-ionic

Cationic polyelectrolytes are active in a field with acid or neutral pH, those in the second group in an alkaline pH field, those in the third group will work in either field, provided that pH it is not too far from neutrality.

Sometimes, polyelectrolytes act alone, but they often work as an adjuvant of other flocculants of inorganic nature (normally metal salts).

The reason for this lies in the fact that metal ions form a floc which gests bigger with the addition of polyelectrolytes (which react with the "zeta" potential, see theory) and, as they settle, drag along lighter or colloidal particles which otherwise might remain dispersed in the liquid phase above.

In the specific case in question, since the solution already contains trivalent metal ions (i.e. Cr^{3+}), we may presume that it is not indispensable to add any metal flocculant. However, it is interesting to assess the influence of this addition to the flocculation process and therefore the experience will involve a number of tests concerning both the identification of the most effective type of polyelectrolyte and the influence of added metal ions (in addition to those already contained in the water to be treated).

In this experience, which is only designed to determine the type of flocculant to be added, the other parameters are maintained unaltered with the following values:

- quantity of flocculant: 5 ppm (corresponding to 350 mg for our 70 lt. of water)
- pH of the medium: 8.5
- degree of dilution: 0.035% (it takes one litre of solution)
- add-in rate: 500 cc/h, and at all events, a rate ensuring that the solution is added at an even pace, over a time period corresponding to the passage of the 70 lt. of water to be treated.

In view of the basic nature of the solution to be treated, we must proceed with anionic or non-ionic polyelectrolytes.

At all events, a number of tests will also be performed with a cationic flocculant in order to assess the applicability of these adjuvants.

For this experience we are using flocculants produced by THE DOW CHEMICAL COMPANY, a company that is present on the Italian market through UNIONE CHIMICA EUROPEA.

The polyelectrolytes selected for the tests are:

AP273, AP30, AP45; MG200; CP35 all of them with registered mark SEPARAN ®

® A trademark of THE DOW CHEMICAL COMPANY.

Dissolution and solution preparation modalities:

Prepare a 0.5% starting solution by adding the polyelectrolyte to the water in small quantities while stirring all along. When the solution has become clear and homogeneous you can dilute it with water to the desired concentration.

4.4.1 Execution of the test

Perform experience no. 1 up to point "o" then start adding flocculant and monitor settling velocity. Perform the experience using all the types of polyelectrolytes available and listed above; complete the table below with the analytical and the experimental data obtained.

Type of polyelectrolyte	***Settling time***	***Dry concentration of sludge***	***% solid in suspension***
Without flocculant			
AP 273			
AP 45			
AP 30			
MG 200			
CP 35			

Based on the values measured and entered in the table we can choose the most appropriate type of polyelectrolyte and then use it to perform another experience according to the same modalities and using, in addition to the polyelectrolyte, one litre of 0.35% ferric chloride solution; in this manner, we shall have added 3500 mg of salt to the 70 litres of H_2O to be treated with a concentration of 50 ppm (mg/1).

The checks to be performed at the end of this test include: settling velocity, dry concentration of the sludge, percentage of solids in suspension. The results obtained must be compared in order to assess the influence - if any - of the addition of a flocculant consisting of a trivalent metallic ion.

4.5 Experience no. 4 - Influence of the pH of the medium on the flocculation process

Having identified in Experience no. 5 the most effective type of polyelectrolyte, with this experience we shall assess the influence of the pH of the medium on the effectiveness of the flocculation process, leaving the other process parameters unaltered, i.e.:

- quantity of flocculant: 5 ppm (corresponding to 350 mg for 70 litres of water)
- degree of dilution: 0.035% (it takes one litre of solution)
- add-in rate: 500 cc/h, and at all events, a rate ensuring that the solution is added at an even pace, over a time period corresponding to the passage of the 70 lt. of water to be treated
- type of polyelectrolyte: the one identified in Experience no. 4

Modalities of dissolution and preparation of the polyelectrolyte solution:

- prepare a 0.5% starting solution by adding the polyelectrolyte to the water in small quantities while stirring all along. When the solution has become clear and homogeneous you can dilute it with water to the desired concentration.

4.5.1 Execution of the test

Perform all the steps described under experience no. 1, up to point “h”, then calibrate the pH instrument. Do this several times, starting from a pH value of 7.5 and ending with pH 12, in 0.5 increments. Initially do not make any other changes to Experience no. 1, then repeat it with the same pH increments but adding the polyelectrolyte as described in Experience no. 4.

Enter the results obtained into the chart, using the following schemes.

Each of the two diagrams will show two curves: one corresponding to the tests without polyelectrolyte and another with the polyelectrolyte.

Thus we shall be able to assess the effectiveness of the flocculant (if the test has been performed with care, the dotted line must be above the solid line at least from pH 8 upwards) and we shall be able to identify the most appropriate pH.

To this end, it is necessary to keep in mind that according to the current regulations on water pollution, the pH of effluents must be comprised between 6.5 and 8.5 so that, if it proves necessary to work at pH 8.5, it will then be necessary to subject the clarified water to a further process of neutralisation.

This suggests that, if there is no appreciable difference in behaviour, it is more advisable to work at a pH that will remain within the legal limits so as to avoid a further process and the ensuing increase in system costs.

In conclusion, it is preferable to limit the pH value to ≤ 8.5, even if at higher values the process would be more effective.

Naturally this applies only if the difference in behaviour is not excessive.

4.6 Experience no. 6 - Influence of the quantity of polyelectrolyte on flocculation

Having identified through experiences 4 and 5, the best type of polyelectrolyte and the best pH value, with this experience we shall assess the quantity of flocculant to be used, leaving the other process parameters unaltered, and namely:

- polyelectrolyte dilution: 0.035%;
- add-in rate: 500 cc/h, and at all events, a rate ensuring that the solution is added at an even pace, over a time period corresponding to the passage of the 70 lt. of water to be treated;
- type of polyelectrolyte: as identified in Experience no. 4;
- pH of the medium: as identified in Experience no. 5.

Modalities of dissolution and preparation of the polyelectrolyte solution:

Prepare a 0.5% starting solution by adding the polyelectrolyte to the water in small quantities while stirring all along. When the solution has become clear and homogeneous you can dilute it with water to the desired concentration.

Since the concentration of the polyelectrolyte solution used is kept constant, the quantity of solution added will necessarily have to be changed in order to be able to vary the percentage of polyelectrolyte. As a rule, when the quantity of polyelectrolyte increases this achieves an improvement in the flocculation process or even, beyond certain values, its stabilisation; however, the curve reflecting process efficiency will rarely undergo a decrease, hence the aim of this experience to determine the minimum quantity of flocculant. We want to know this because the price of polyelectrolytes commonly used is rather high and hence we want to use the minimum quantity: the cost of polyelectrolytes being approx. 2500 lire/kg it is obvious that even one ppm more than is technically necessary will give rise to an increase in costs of 2.5 lire per m^3 of water to be clarified.

4.6.1 Execution of the test

Perform Experience no. 4 in its entirety, but at point “o” vary the quantity of flocculant solution employed to carry out a series of experiences with polyelectrolyte quantities ranging from 1 to 6 ppm; change the quantity in 0.5 ppm steps.

Plot the results in the charts, using the schemes given below.

The interpretation of the two charts will make it possible to identify the minimum quantity needed.

4.7 Experience no. 7 - Influence of the degree of dilution of the polyelectrolyte on the flocculation process

Having identified, through Experiences 4, 5 and 6, the best type of polyelectrolyte, the appropriate quantity of polyelectrolyte, and the ideal pH of the medium, with this experience we want to assess the degree of dilution of the polyelectrolyte solution, while leaving the other process parameters unaltered, and namely:

- add-in rate: a rate ensuring that the solution is added at an even pace, over a time period corresponding to the passage of the 70 lt. of water to be treated;
- type of polyelectrolyte: as identified in Experience no. 4;
- pH of the medium: as identified in Experience no. 5.
- quantity of flocculant: as identified in Experience no. 6

Modalities of dissolution and preparation of the polyelectrolyte solution.

It is good practice to prepare a 0.5% starting solution and from this produce the solutions to be used, so as to have a series of solutions from 0.01 to 0.05% with concentration intervals of 0.005%.

4.7.1 Execution of the test

Since the amount of flocculant employed is kept constant, in order to assess the degree of dilution we shall vary the quantity of solution added.

First of all, perform Experience no. 6 in its entirety; at step “o” add the flocculant solutions at different concentrations but make sure that the dosage is the same in each test.

Plot the results obtained in the charts according to the following schemes:

- the interpretation of the two charts will make it possible to identify the optimal concentration.
- the degree of dilution fosters the finest possible dispersion in the water to be treated, increasing the contact surface.

4.8 Experience no. 8 - Influence of the simultaneous variation of type of polyelectrolyte and ph of the medium on the flocculation process

As a rule, polyelectrolytes display a behaviour that varies to a significant extent depending on the pH of the medium; actually, in some cases, they will be totally inactive at a given pH (even if the latter remains within the limits of validity for the type of polyelectrolyte employed) whereas with a variation of but 0.5 in pH the activity of the electrolyte may be appreciably enhanced.

Accordingly, it was deemed worthwhile to test out the action of different polyelectrolytes (of anionic type, in this particular case) as a function of pH, by repeating Experience no. 5 in its entirety for each polyelectrolyte tested and entering the results in the two tables reproduced below:

pH	Type of flocculant		

Settling velocity

pH	Type of flocculant		

dry % of sludge

4.9 Experience no. 9 - Chemical evaluation of pollutants contained in the water before and after the treatment plant

Having identified the most effective flocculation method, it is important to determine the effectiveness of the entire treatment. Accordingly, we shall perform a number of analytical determinations in order to assess the degree of effluent clarification achieved.

For the sake of clarity, we have produced a table showing the limits of acceptability of the effluents, as provided for by most local bodies. *(insert table*)

Naturally, for the various experiences suggested it will not be necessary to perform all the checks, but only those relating to the elements that may be a cause of pollution.

The aspects to be checked include the following:

- pH, in order to determine the functionality of the pH-meter (instrument 78);
- settling substances: to asses the functionality of the settling tank (5)
- substances in suspension: to assess the validity of the flocculation process (limited to Experiences nos. 1-3-4-5-6-7).
  - Hexavalent chrome
  - Trivalent chrome
  - Cyanides (limited to Experience no. 2)
  - Iron: if ferric chloride is used as a flocculant agent.

Settling substances

Settling substances are the solids suspended in the effluents at the time of discharge that can settle over a time period of up to two hours. The result is expressed in terms of cc of substances settled per litre of water.

The equipment used is Ihmoff's cone (option), which is a 1 litre capacity glass vessel with a graduated scale in millilitres.

The water to be treated is homogenised by energetic stirring and then is introduced into Imhoff's cone (option).

To have an idea of settling velocity it is good practice to take readings of the volume of substances sedimented after 45', 1h, 1h and 30', and then take a final reading after 2h.

Substances in suspension

These are the solid substances that are found in suspension in the water and do not settle of their own accord during a 2 hour time period.

To measure them, we have to collect them on a filter and weigh them; the result is expressed in mg per litre of water.

The working procedure is as follows:

- Wash a cellulose filter of appropriate porosity, dry it in an oven at 105°C and, after cooling it in a drier, weigh it.
- Pass through a calibrated filter a volume V of the water in question, after homogenising it by rapid stirring.
- Dry the filter in an oven at 105°C until its weight is stabilised, cool it in a drier and weigh it.
- Let us denote with P the weight obtained, with Po the weight of the filter and with V the volume of water filtered (in ml); the substances in suspension (in mg/lt) are obtained through the following formula:

$$substances\ in\ suspension\ in\ \ mg/lt = \frac{(P - Po)\cdot 1000}{V}$$

4.10 Experience no. 10 - Dosing hexavalent and trivalent chrome

Cr^{6+} is dosed through the calorimetric method using diphenylcarbazide as an indicator: we get a red-purple colouring.

Reactants needed: (freshly made)

- Bidistilled water
- Diphenylcarbazide solution
  - diphenylcarbazide (analytically pure) g. 0,2
  - ethylic alcohol at 95° ml 100
  - sulphuric acid 1 : 10 ml 400
- Sample solution of hexavalent chrome, 1 mg/l

To perform the test it is necessary first of all to plot the calibration curve with known titre solutions of Cr^{6+}.

The samples are prepared by placing increasing quantities of the sample chrome solution in calibrated 50 cc volumetric flasks, according to the following table:

Sample solution of conc. 1 mg/l – in ml	0	0.25	0.50	0.75	1	2.5	5	7.5	10
Bidistilled water, in m1	50	49.75	49.50	49.25	49	47.5	45	42.5	40
Diphenylcarbazide solution in m1	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Chrome content, in mg/l	0	0.005	0.010	0.015	0.02	0.05	0.1	0.15	0.20

Let the reactants rest for 10' to enable the colouring to develop fully, then measure with a colorimeter (or a spectrophotometer) with 540 mm wave length.

With the data obtained we plot the Cr^{6+} cnc./extinction curve.

Through the same modalities, repeat the reading with the water being examined and work out the chrome content directly from the curve.

Total chrome dosage is performed by oxidising Cr^{3+} and Cr^{6+} and then performing the determination process as in the previous case. This gives the sum of Cr^{3+} + Cr^{6+}: subtract from this value the one obtained before for Cr^{6+} alone to obtain the value of Cr^{3+}.

The oxidation of Cr^{3+} requires the following reactants (freshly made):

- sulphuric acid 1:2
- sodium sulphite solution:
  - sulphite solution (analytically pure) gr. 1.26
  - bidistilled water ml 100
- potassium permanganate solution:
  - potassium permanganate gr. 0,632
  - bidistilled water ml 100
- sodium azide solution:
  - sodium azide gr. 0.5
  - distilled water ml 100

The procedure consists of reducing Cr^{6+} to Cr^{3+}, oxidising all the Cr^{3+} and Cr^{6+} and then determining it colorimetrically. Place 25 cc of the water to be analysed in a 250 cc flask, then add 5 cc of 1:2 sulphuric acid and 1 cc of the sodium sulphite solution. Heat to ca 90°C for 5 minutes and dilute with 20 cc of bidistilled H_2O, then bring to a boil; add the solution of $KmnO_4$ in drops until a persistent pink colouring is obtained, boil for 10 minutes. Eliminate excess $KmnO_4$ with the sodium azide solution paying attention not to add too much, then boil for another 2 minutes.

Cool and place 50 cc in a calibrated volumetric flask.

Determine the quantity of Cr^{6+} through the calorimetric method.

Determination of cyanides

Cyanides are determined volumetrically, after distilling them in the presence of H_2SO_4 and collected in the form of alkaline cyanides in a KOH solution.

This initial operation is performed in a type Kjeldah1 device by pouring into the flask 250 cc of the water to be examined and adding in drops 25 cc of concentrated H_2SO_4.

Distil for one hour by bubbling the distillate in 50 cc of KOHN; the cyanide acid is then collected as N_aCN.

At this point, the alkaline cyanide solution is tritrated with $AgNO_3$ 0.1 N using dimethylaminobenzalrhodamine as an indicator (0.02% solution in acetone). In lieu of dimethylaminobenzalrhodamine it is possible to use KI in 10% solution.

The Ag^+ ions added in the previous step combine with the CN^- to form a soluble complex: when all the CN^- have reacted, the addition of a small excess quantity of AG^+ causes the dimethylaminobenzalrhodamine to turn salmon pink or the AgI precipitate to turn light yellow.

Denoting with A the quantity of $AgNO_3$ 0.1N (in cc) used in 250 cc of water, the CN^- content (in mg/lt.) is given by the following relationship:

$$\frac{A \cdot 5.2 \cdot 1000}{250}$$

Determination of iron

The determination of iron is performed through the colorimetric method based on the reddish colour taken on by ferrous salts in the presence of orthophenanthroline.

The reactants to be used, dissolved in bidistilled water, without any trace of iron, are as follows:

- HC1 N solution
- saturate solution of sodium acetate
- 1% ascorbic acid solution, freshly made
- freshly made solution of orthophenanthroline
- starting solution of 1 gr/lt. of iron (weigh exactly 100 mg of iron filings, pure and washed with ether, dissolve in flasks with 10 cc of HNO_3 conc. + 40 cc of water. In a volumetric flask adjust volume to 100 cc)
- 0.1% iron solution (this is produced by diluting to 1:10 the previous solution).

To perform the calibration curve take various samples, from 0.1 to 1 cc, of the known titre iron solution (containing 0.1% iron), add 1 cc of the NC1/N solution, 0.5 cc of the saturate sodium acetate solution, 0.3 cc of the 1% ascorbic acid solution and 1 cc of the 0.1% orthophenanthroline solution. The samples taken from the known titre solution being, for instance, 0 cc (no load test) 0.1 – 0.2 – 0.4 – 0.6 – 0.8 – 1, adjust the volume of each sample taken plus the different reactants added to the same value by adding 10 – 9.9 – 9.8 – 9.6 – 9.4 – 9.2 –9 cc of bidistilled water, respectively.

The iron content in the starting solution being 0.1% the percentage of this metal contained in each sample will be 0 – 0.1 – 0.2 – 0.4 – 0.6 – 0.8 and 1 mg/lt., respectively.

Let the test tubes prepared in this manner rest for 30’ and read them under a spectrophotometer or spectrocolorimeter under a light with 51 Ohm wave length. Plot the calibration curve from the values obtained.

Now take a 10 cc sample of the water to analysed, add 1 cc of HC1 N and bring to a boil; let it cool, restore the volume to the initial 10 cc, add 0.5 cc of the sodium acetate solution, 0.3 cc of the ascorbic acid solution and 1 cc if the orthophenanthroline solution.

In this case too, prepare a no load test starting with 10 cc of bidistilled water and, as usual, use it to reset the instrument.

The result is expressed in mg/lt. of iron.

Settling substances

Settling substances are the solids suspended in the effluents at the time of discharge that can settle over a time period of up to two hours. The result is expressed in terms of cc of substances settled per litre of water.

The equipment used is Ihmoff's cone (option), which is a 1 litre capacity glass vessel with a graduated scale in millilitres.

The water to be treated is homogenised by energetic stirring and then introduced into Imhoff's cone (option).

To have an idea of settling velocity it is good practice to take readings of the volume of substances sedimented after 45', 1h, 1h and 30', and then take a final reading after 2h.

Substances in suspension

These are the solid substances that are found in suspension in the water and do not settle of their own accord during a 2 hour time period. To measure them, we have to collect them on a filter and weigh them; the result is expressed in mg per litre of water.

The working procedure is as follows:

- Wash a cellulose filter of appropriate porosity, dry it in an oven at 105°C and, after cooling it in a drier, weigh it.
- Pass through a calibrated filter a volume V of the water in question, after homogenising it by rapid stirring.
- Dry the filter in an oven at 105°C until its weight is stabilised, cool it in a drier and weigh it.
- Let us denote with P the weight obtained, with Po the weight of the filter and with V the volume of water filtered (in ml); the substances in suspension (in mg/lt.) are obtained through the following formula:

$$\textit{substances in suspension in mg/lt.} = \frac{(P - Po) \cdot 1000}{V}$$

4.11 Experience no. 11 - Crystallisation studies

In this experience we shall examine the phenomenon of crystallisation by cooling starting from a hot saturate solution.

This experiment can be performed on a solution of any salt; we shall exemplify the procedure with a saturate solution of copper sulphate.

The solubility curve can be worked out from the following table:

Temperature	Crystallised copper sulphate dissolved in 100 cc. of H_2O [gr.]
0°	31.6
10°	36.9
20°	42.3
30°	48.8
40°	56.9
50°	65.8
60°	77.3
70°	94.0
80°	118.0
90°	156.4
100°	203.3

In the tank used to prepare the solutions of the water to be treated, prepare a salt solution at a temperature of between 50 °C and 70 °C.

Transfer the solution to the the tank equipped with a coil in which the coolant is circulated.

This will cause a crystallisation process and the water containing the crystals will be transferred to the settling tank.

At this point, settling velocity can be determined as a function of crystal size, which, in its turn, depend on cooling rate.

Several experiments can be performed at this point by varying the following parameters, either singly or in combination:

a) temperature at the inlet of the coolant;

b) coolant flow rate;

c) flow at the settling tank.